

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 903 424 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
24.03.1999 Bulletin 1999/12

(51) Int. Cl.⁶: C23C 26/00

(21) Application number: 98117232.3

(22) Date of filing: 11.09.1998

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 19.09.1997 US 59538 P

(71) Applicant: Haldor Topsoe A/S
DK-2800 Lyngby (DK)

(72) Inventors:
• Alstrup, Ib
2840 Holte (DK)
• Chorkendorff, Ib
3460 Birkerød (DK)

(54) Corrosion resistance of high temperature alloys

(57) A method for enhancing the protection of high temperature alloys containing iron, nickel and chromium against high temperature corrosion by carburization or metal dusting comprising:

(a) deposition of a thin layer of a metal selected from one or more of the noble metals, precious metals, metals from group IV and group V of the Periodic Table and mixtures thereof with a thickness in the range 0.01 to 10 µm on the surface to be protected.

(b) annealing of the treated surface in an inert atmosphere at a predetermined temperature for a sufficient time.

EP 0 903 424 A1

Description

[0001] The present invention relates to a method for protecting high temperature alloys containing iron, nickel and chromium against high temperature corrosion caused by carburization or metal dusting.

Background of the Invention

[0002] It is a major problem in many industrial processes that the high temperature alloys commonly used as construction materials are susceptible to corrosion by oxidation or carburization or metal dusting when exposed at high temperatures to gases with a high carbon potential. Carburization is observed in the petrochemical industry, where ethylene is produced in pyrolysis furnaces by thermal cracking of hydrocarbons in a steam-hydrocarbon mixture at temperatures up to 1100°C. In this cracking process, coke deposition occurs at the inner walls of the cracking tubes. In steam reformers, natural gas or other hydrocarbons are converted by catalytic reaction on nickel catalysts to CO and H₂. Carburization of the tube walls is observed after overheating or excessive carbon activities. In industrial furnaces for heat treatment or carburization of steels, carburization of the carrying grates and of the furnace walls also occurs. Components of the CO₂-cooled nuclear reactor may be carburized by CO₂, and the heat exchangers of the helium-cooled reactor may be carburized by impurities such as CO and CH₄ in the helium. In coal gasification and in waste incineration plants, carburization is possible but the sulphidation and corrosion by chlorine will be more severe. Downstream of the steam reforming furnace, the heat recovering equipment is potentially vulnerable to a severe form of corrosion known as 'metal dusting'. It is a catastrophic carburization process to which alloys containing iron, nickel and cobalt is vulnerable, which results in the disintegration of the alloy into 'dust' consisting of particles of carbon, carbides, metal and oxides. The result is wastage of the alloy surface. In contrast to the above mentioned carburization, metal dusting occurs at temperatures as low as approximately 450°C. As a result of many studies, it has been concluded that virtually all available high temperature alloys are vulnerable to metal dusting. It has been shown that addition of H₂S to the gas may provide some resistance towards carburization and metal dusting. However, because of the risk of undesirable effects, such as catalysts poisoning, this cannot be used in many cases. Efficient means, generally applicable, for protecting such alloys against high temperature corrosion have until now not been developed.

[0003] Usually the protection of high temperature alloys against corrosion is dependent on the formation of an outer chromium-oxide layer. However, such an oxide layer may, under most practical conditions, not be protective for a very long time, because cracks can eas-

ily be formed in the oxide layer and spallation may occur due to loss of adherence to the underlying alloy. The same risks are present when a similar protection is attempted by coating the alloy surface with a protecting mixed oxide layer.

[0004] The method of the present invention does not suffer from such risks, because it does not depend on the formation of a surface oxide layer with thermal and mechanical properties vastly different from those of the alloy.

Summary of the Invention

[0005] In accordance with the present invention there is provided a method for protecting parts and components of industrial plants such as containers, tubes, ferrules, etc. made of high temperature alloys containing iron, nickel and chromium against corrosion by carburization or metal dusting. The method comprises: (a) cleaning of the alloy surface, (b) deposition of a thin layer of a noble or precious metal or of an element from group IV (i.e. Sn and Pb) or from group V (Sb and Bi) on the surface, and (c) heating of the surface in an inert atmosphere to a predetermined temperature period of time to obtain a uniform distribution of the noble or precious metal on and in the surface to be protected.

[0006] Deposition of the above metals may be carried out by conventional methods including physical or chemical vapour deposition or dipping, spraying or plating.

Examples

[0007] The following examples serve to describe the manner of making and using the above mentioned invention in detail.

[0008] A number of metal dusting corrosion tests were carried out using as test samples cylindrical disks with a diameter of approximately 18 mm and thickness of 6 mm made of Alloy 800 H with following composition in wt%:

45 0.05-0.1 C, max. 1.0 Si, max. 1.5 Mn, max. 0.015 S,
 30.0-35.0 Ni, 20.0 Cr, 45 Fe, 0.15-0.6 Ti, 0.15-0.6
 Al, max. 0.75 Cu.

Example 1

50 [0009] Test samples have been tested for metal dusting corrosion at the following conditions:

Gas pressure	: 34 bar
Gas composition	: 49.3% H ₂ , 15.6% CO, 5.6% CO ₂ , 29.5% H ₂ O
Gas velocity	: max. 10 m/s
Sample temperature	: 650°C
Duration	: 200 h

[0010] Tests have been carried out after no surface treatment and after a number of different conventional pretreatments comprising polishing and cleaning of the surface, mechanical treatment, and oxidation of the surface. The mechanical treatments used are sandblasting and shot peening. In all these cases severe metal dusting attacks, i.e. carbon formation, pitting and loss of material were observed after a test. However, when the test sample was pretreated in accordance with the present invention no sign of corrosion could be seen on the pretreated surface after the above mentioned metal dusting corrosion test.

[0011] The following pretreatment was used: The surface was polished and cleaned. An approximately 1 μm thick gold layer was deposited by physical vapour deposition on the surface to be protected. Finally, the sample was kept at 900°C for 30 min. in a flow of helium.

Example 2

[0012] An alloy 800 H test sample with the above mentioned composition has been tested at the following conditions:

Gas pressure	:	34 bar	25
Gas composition	:	39.4% H ₂ , 37.2% CO, 1.7% CO ₂ , 21.7% H ₂ O	
Gas velocity	:	max. 10 m/s	
Sample temperature	:	653°C	
Duration	:	100 h	30

[0013] The following pretreatment was used before the test:

[0014] The sample surface was polished and cleaned. At approximately 3 μm thick tin layer was deposited electrochemically on the surface. The sample was kept at 800°C for 30 min. in a flow of helium.

[0015] No sign of corrosion could be seen on the pretreated surface after the metal dusting corrosion test.

Claims

1. A method for enhancing the protection of high temperature alloys containing iron, nickel and chromium against high temperature corrosion by 45 carburization or metal dusting comprising:

(a) deposition of a thin layer of a metal selected from one or more of the noble metals, precious metals, metals from group IV and group V of the Periodic Table and mixtures thereof with a thickness in the range 0.01 to 10 μm on the surface to be protected.

(b) annealing of the treated surface in an inert atmosphere at a predetermined temperature for a sufficient time.

2. The metal of claim 1, wherein the group IV metals are Sn and/or Pb.
3. The method of claim 1, wherein the group V metals are Sb and/or Bi.

10

15

20

25

35

40

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 98 11 7232

DOCUMENTS CONSIDERED TO BE RELEVANT																		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)															
A	WO 94 15896 A (CHEVRON RES & TECH. CO, SAN FRANCISCO, US) 21 July 1994 * page 14, line 7 - line 17 * * page 17, line 13 - line 27 * * page 18, line 22 - page 19, line 6 * * claims 45,46 * ---	1-3	C23C26/00															
A	DE 24 39 739 A (CZEPEK & CO, HAUSEN, DE) 4 March 1976 * page 1, line 1 - line 23 * * page 3, line 25 - line 35 * ---	1,2																
A	DATABASE WPI Section Ch, Week 8122 Derwent Publications Ltd., London, GB; Class J08, AN 81-39357D XP002090077 & JP 56 018876 B (INOUE JAPAX RES INC) , 1 May 1981 * abstract * ---	1																
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 373 (C-391), 12 December 1986 & JP 61 166987 A (HITACHI CABLE LTD), 28 July 1986 * abstract * ---	1-3	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C23C															
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 310 (C-379), 22 October 1986 & JP 61 119678 A (NIPPON STEEL CORP), 6 June 1986 * abstract * -----	1,2																
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search</td> <td>Date of completion of the search</td> <td>Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>14 January 1999</td> <td>Peis, S</td> </tr> <tr> <td colspan="3">CATEGORY OF CITED DOCUMENTS</td> </tr> <tr> <td colspan="3"> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document </td> </tr> <tr> <td colspan="3"> T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document </td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	14 January 1999	Peis, S	CATEGORY OF CITED DOCUMENTS			X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document		
Place of search	Date of completion of the search	Examiner																
THE HAGUE	14 January 1999	Peis, S																
CATEGORY OF CITED DOCUMENTS																		
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document																		
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document																		

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 98 11 7232

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information..

14-01-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9415896 A	21-07-1994	AU 6161094 A CA 2153231 A CN 1119430 A EP 0677034 A JP 8505621 T US 5849969 A	15-08-1994 21-07-1994 27-03-1996 18-10-1995 18-06-1996 15-12-1998
DE 2439739 A	04-03-1976	NONE	

THIS PAGE BLANK (USPTO)